Magnetism in pristine pi-conjugated polymers

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14. ABSTRACT

In this study, the magnetic and magneto-optic properties of π-conjugated polymers were investigated. This research was initiated by the observation of extremely strong Faraday rotation in films of pristine highly regioregular poly(3-alkylthiophene)s and subsequently a ferromagnetic hysteretic behavior at low temperature (< 20K) in these polymers. Concomitantly nanoscopic doughnut structures (diameter ~12 nm) were observed in such thin films spin coated from a poor solvent (toluene). Interestingly all such properties and structures were absent from regiorandom poly(3-alkylthiophene)s. Over the course of the project, we developed an extended portfolio of polythiophenes, achiral as well as chiral, which have been thoroughly characterized in their chemical properties. Faraday measurements on these polymers, in solution and thin films, have clearly shown the great potential of these polymers as materials for magneto-optical applications. The results of this project have also opened a new way to organic magnetism of environmental stable polymers, while on a more theoretical way the study of persistent currents in organic cyclic structures has been initiated.

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Magnetism in pristine π-conjugated polymers

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Abstract and Summary of Project-Objectives.

The objectives of the proposal "Magnetism in pristine π-conjugated polymers" are the investigation of the magnetic and magneto-optic properties of π-conjugated polymers. This research was initiated by the observation of extremely strong Faraday rotation in films of pristine highly regioregular poly(3-alkylthiophene)s and subsequently a ferromagnetic hysteretic behavior at low temperature (T < 20k) in these polymers. Concomitantly nanoscopic doughnut structures (Ø ~12 nm) were observed in such thin films spin coated from a poor solvent (toluene). Interestingly all such properties and structures were *absent* from regiorandom poly(3-alkylthiophene)s.

All these observations led us to the working hypothesis that the magnetic properties in the regioregular poly(3-alkylthiophene)s are linked to these nanoscopic doughnut supramolecular structures and which may only be feasible in the regioregular polymers due to specific spatial requirements. To understand the formation of such doughnut structures we advanced the hypothesis that the doughnuts, as observed by AFM in thin films spin-coated from toluene on silicon, are formed from micellar structures present in solutions of the polymers, especially in poor solvents. [See Figure 1 for the doughnuts and ferromagnetic transition in regioregular poly(3-dodecylthiophene, key references given in the References].
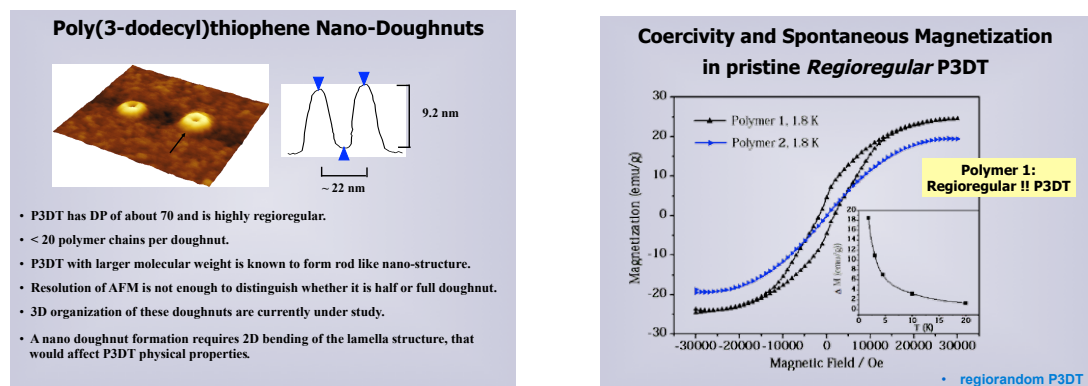
Figure 1. a) Doughnut structure in thin film of pristine regioregular poly(3-dodecylthiophene) and b) ferromagnetic transition at 1.8K (compare absence in regiorandom polymer).

New directions

As seen from the abstract the most important issue for this project is the ferromagnetic transition in poly(3-alkylthiophene)s - Fig 1b –, which may be a completely new approach to organic magnetism in pristine polymers with good environmental stability. The project strongly focused therefore on cyclic structures, with a theoretical description, as well as on an experimental approach involving the synthesis of macrocycles of 3-alkylthiophenes. These investigations may be instrumental in the explanation of the physical basis of the giant Faraday rotation observed in thin films of poly(3-alkylthiophene)s.

Synthesis

In view of the previous results the research efforts mainly focused on the synthesis of new π-conjugated polythiophenes and more in particular, on block copolymers composed of one achiral poly(3-alkylthiophene) (P3AT) and one chiral poly(3-alkoxythiophene) (P3AOT) or P3AT block. Here we are expecting an enhancement of micelle formation. Apart from their synthesis, also the aggregation behavior was studied into detail using UV-vis and CD spectroscopy, as this most probably influences the Faraday rotation of the material.

Two classes of block copolymers were prepared: block copolymers composed of an achiral and chiral P3AT block (P3AT*-*b*-P3AT) and block copolymers composed of a chiral P3AOT and a achiral P3AT block (P3AOT*-*b*-P3AT). In the former block-copolymers, the blocks are directly connected to each other, while in the latter a flexible alkyl spacer of varying length between the blocks is present.

P3AT*-*b*-P3AT

The synthesis of the block copolymers was performed using a two-step procedure exploited the controlled chain-growth polymerization of P3ATs (Figure 1). The polymers were prepared using the well-known Ni(dppp)-mediated protocol, also called the catalyst transfer polymerization. In this protocol Ni(dppp)Cl$_2$ or an externally prepared aryl(diphenylphosphinopropane)nickel bromide catalyst is added to a monobromo-monochloromagnesiothiophene monomer. After consumption of the first monomer the second monomer is introduced, forming the block-copolymers. The length of the respective block was varied by adjusting the amount of monomer added. More in particular, the total number of thiophene monomers was fixed at 40, while the length of the blocks was varied by adjusting the ratio monomer/initiator.
A key element in this polymerization protocol is the complexation of the Ni-catalyst to the π-system of the conjugated polymer backbone and the "walking" of this catalyst along the polymer backbone. Hence, the catalyst can "walk back" to the initial beginning of the backbone. If Ni(dppp)Cl$_2$ is used, a copolymerization would result in BAB triblock copolymers instead of AB diblock copolymer. Therefore, o-totyl(diphenylphospinopropane)nickel bromide was used as a catalyst.
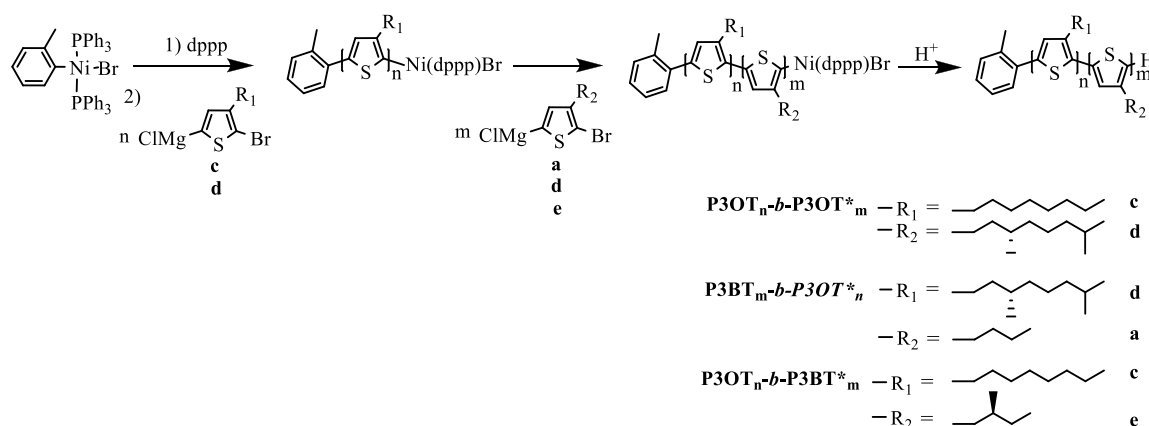
Figure 2. Synthesis of the P3AT*-b-P3AT block copolymers

The molecular structure and composition of the block copolymers was verified by NMR spectroscopy.

The degree of polymerization/molar mass was determined both by NMR spectroscopy (quantification of the end groups) and gel permeation chromatography (GPC). This confirmed the targeted degree of polymerization (i.e. 40). The polydispersity was low in all cases (1.1-1.2).

Next, solvatochromism experiments were performed on the polymers. For this purpose, the polymers were dissolved in chloroform and methanol, a nonsolvent was gradually added. If a clear difference in solubility between the two blocks is present, one block aggregates first, followed by the second block at high nonsolvent content. If, however, the solubility of both blocks is more or less the same, both block aggregate at the same time. Since one block is chiral, this block might aggregate in a chiral way. The chiral response was evaluated by calculating the g-value (g-value = $\Delta\varepsilon/\varepsilon$) for each polymer and plotting the maximal value in function of the content of chiral monomer (Figure 2). In this way, three different regimes could be distinguished:

- the chiral block aggregates first, followed by the achiral block. This is founded in cases of a long chiral block and a short achiral block (green and black line at high chiral content). In that case, the chiral block imposes its chiral supramolecular structure to the achiral block resulting in a chiral stacking of both blocks. This gives rise to a chiral supramolecular structure that is similar to that of the chiral homopolymer and, indeed, more or less the same g-value is found.
- the achiral block aggregates first, followed by the chiral block. This is observed in cases of a long poly(butylthiophene) block and a short chiral block (blue line at low to medium chiral content). In that case, the achiral block imposes its achiral stacking to the chiral block. This results in an overall achiral stacking and thus, a zero g-value.
- both blocks aggregate at the same time. In that case, mixed aggregates or phase-separation occurs. This can be found in case of a rather short achiral block and long chiral block (green and black line at rather low chiral content). Phase-separation can be ruled out, since in that case a g-value similar to that of the chiral homopolymer should be found, which is not the case. Interestingly, a g-value that is much higher

than that of the chiral homopolymers was found, suggesting that chirality is more efficiently expressed in the block copolymers rather than in a chiral homopolymer. This amplification of chirality is unique.
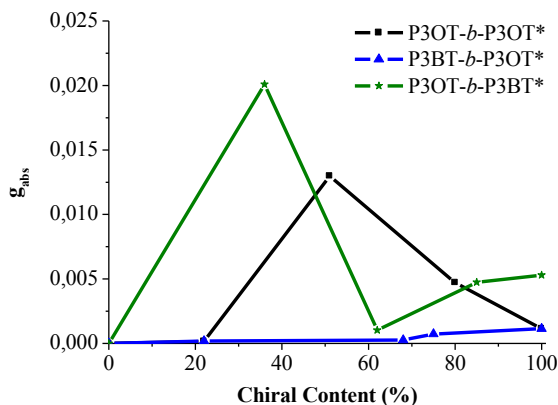

Figure 3. Evolution of the g-value in function of the content of chiral monomer.

P3AOT*-*b*-P3AT

These polymers were prepared in a different procedure. In a first step, the polymers were prepared starting from a functionalized Ni-catalyst. In this way, a P3AOT endcapped with a (protected) acetylene was synthesized and P3ATs endcapped with a protected alcohol functionality. The alcohol was converted to an azide. In a next step, the two homopolymers are coupled using the click reaction (Figure 3). In that way, block copolymers P3AOT*-b-P3AT with a alkyl spacer of different length are obtained.
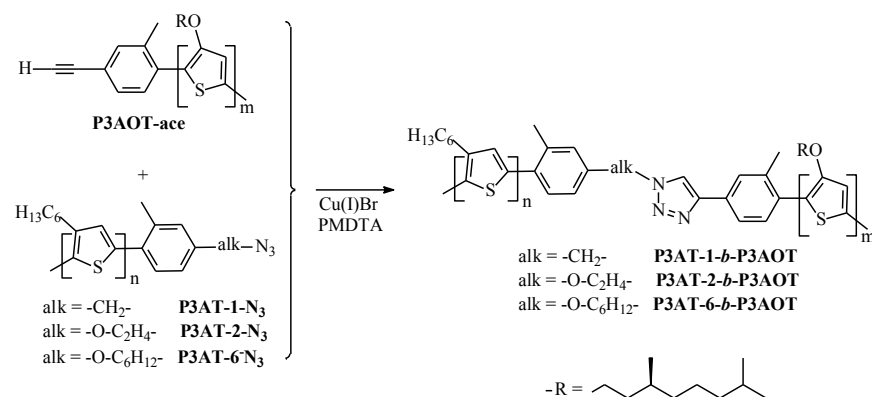

Figure 4. Synthesis of the P3AOT*-*b*-P3AT block copolymers

NMR spectroscopy demonstrated the presence of both blocks, while GPC confirmed that indeed block copolymers were obtained.

Next, solvatochromism experiments were carried out. Since the solubility of P3AOT is lower than that of P3AT, the P3AOT aggregates first. Since the P3AOT block is

equipped with chiral side-chains, it aggregates in a chiral way. The question arises whether the P3AOT can force the achiral P3AT to aggregate in a chiral way, although it is separated from the chiral P3AOT with a flexible alkyl group. If the CD spectra are considered (Figure 4), it is clear that first the P3AOT block aggregates in a chiral way (Cotton effect near 600 nm – the absorption of P3AOT; green and red line). When also P3AT aggregates (blue lines), the CD spectra become a superposition of a bisignate Cotton effect around 600 nm (from the P3AOT) and a bisignate Cotton effect near 530 nm, that corresponds to the absorption band of P3AT. This clearly demonstrates that in all cases the achiral P3AT stacks in a chiral way, even if it separated from the chiral P3AOT with a long, flexible alkyl spacer.
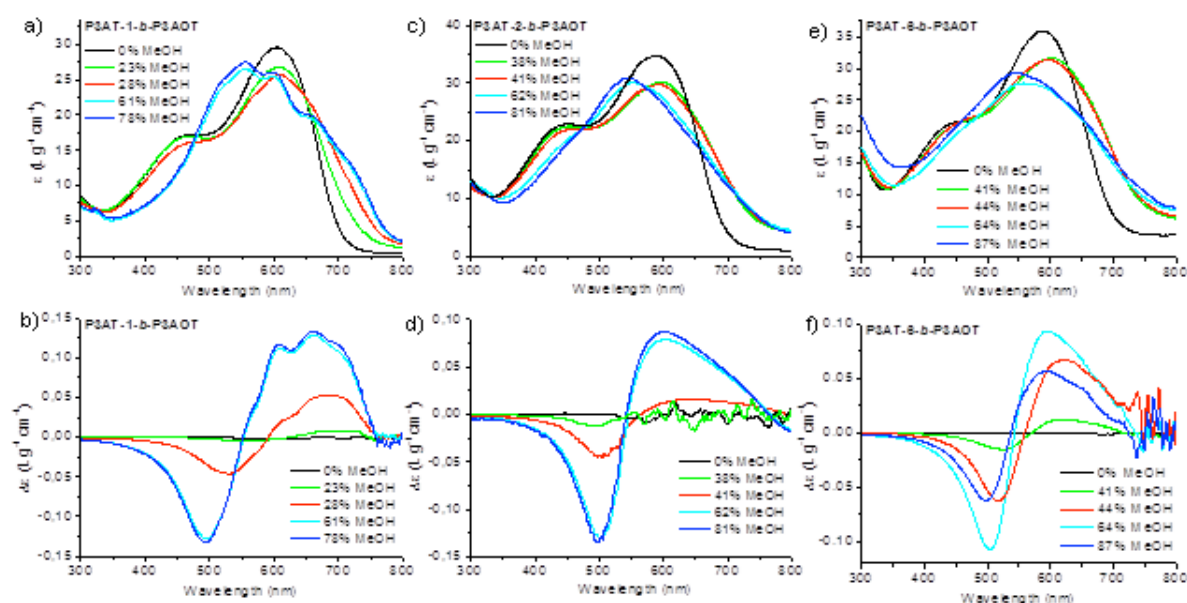

Figure 5. UV-vis (a, c and e) and CD (b, d and f) spectra of the P3AOT*-*b*-P3AT block copolymers

Since the magnetic effects observed in poly(3-alkylthiophene)s are probably related to spin-orbit coupling we synthesized poly(3-alkyl*seleno*phene)s. This was based upon the low-lying filled d-orbitals in selenephene as contrasted to thiophene. Also the Se-atom is about 3x heavier than the sulfur-atom and we could therefore expect much stronger magnetic effects.

The synthesis of a chiral, regioregular poly(3-alkylselenophene) (P3AS) was targeted following well-known procedures:
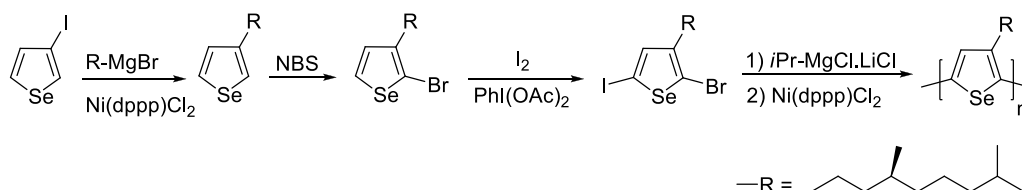
Our synthesis resulted in a polymer with a very high degree of regioregularity – apart from the inevitable presence of one TT-coupling - and no defects were found. From GPC a M_n = 9,9 kg/mol was determined as well as a very low polydispersity of 1.1, indicative for the living polymerization technique used.

In films of polythiophenes we have repeatedly observed a strong dependence of Faraday rotation on the supramolecular organization in the films, most often a result of the preparation of the film by spincoating (temperature, solvent, rotation speed…). The Faraday rotation in films of poly(cyclopentadithiophene) is very strong but fade away over time. This is presumably due to the slow crystallization in the films. From this important, though negative, result it was concluded that amorphous films, no strong chain interactions, would show the highest Faraday rotation. We therefore started the synthesis of statistical copolymers where the tendency of crystallization is reduced:
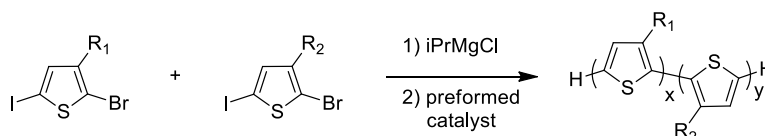
The first choice of statistical copolymers was based upon the copolymerisation of 3-(2-ethylhexyl)thiophenes and 3-dodecylthiophene. According to literature and previous work the polymerisation was easily performed at 35°C.
Homopolymerisation of each monomer at room temperature or 35°C, targeting the same degree of polymerisation, were also carried out. From NMR data (integration of signal) the ratio of ethylhexyl/dodecyl in the statistical copolymer is 45/55, for a target of 50/50. From DSC measurements we concluded that there is still an organization in the polymer and it appears very difficult to obtain amorphous polythiophenes. We will need to develop new synthetic pathways to further decrease the order in the polymer films. All the polymers have high regioregularity.

Table: Macromolecular parameters of homo- and statistical copolymers.

Side chain of monomer	Molar mass theorical	concentration	temperature	Mn (kDa eq. PS standard)	Dispersity	Mp (kDa eq. PS standard)
EthylHexyl	20000	0.2	35°C	10	1.70	20
Dodecyl	25000	0.2	RT	21.1	1.28	30
Dodecyl	25000	0.2	35°C	21.5	1.26	30
EthylHexyl-Dodecyl (50/50)	22500	0.2	35°C	22	1.39	34

To specifically investigate the role of cyclic structures a collaboration was started with he group of Philippe Dubois, University of Mons, Belgium. This group has a strong expertise in the synthesis of polymers and, most important for this project, in the synthesis of macrocycles of 3-alkylthiophenes.

First investigations were started with a macrocycle of regioregular poly(3-hexylthiophene – [O. Coulembier et al., Polym. Chem., 2013, 4, 237], which we call the "Coulembier" ring:
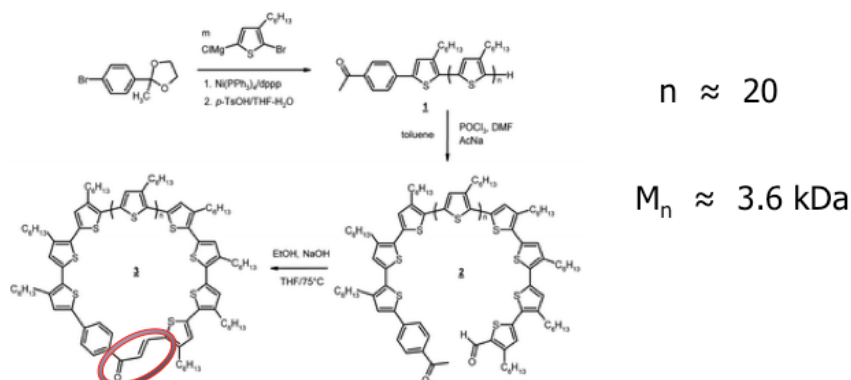

$$n \approx 20$$

$$M_n \approx 3.6 \text{ kDa}$$

Figure 6. The "Coulembier" ring with, in red, the aldol closure

This ring has a diameter of about 5 nm. It is interesting to note that the aldol condensation used to close the ring is breaking the conjugation over the ring – see our results on simulations of this ring.

Together with the Mons group a program was started for synthesis and characterisation of macrocyclic oligothiophenes. As a general approach to the synthesis of macrocycles chain ends of oligomers and polymers were brominated (α,ω-brominated regioregular oligo- and polythiophenes) with the aim of ring closure by Yamamoto or Ullmann coupling:
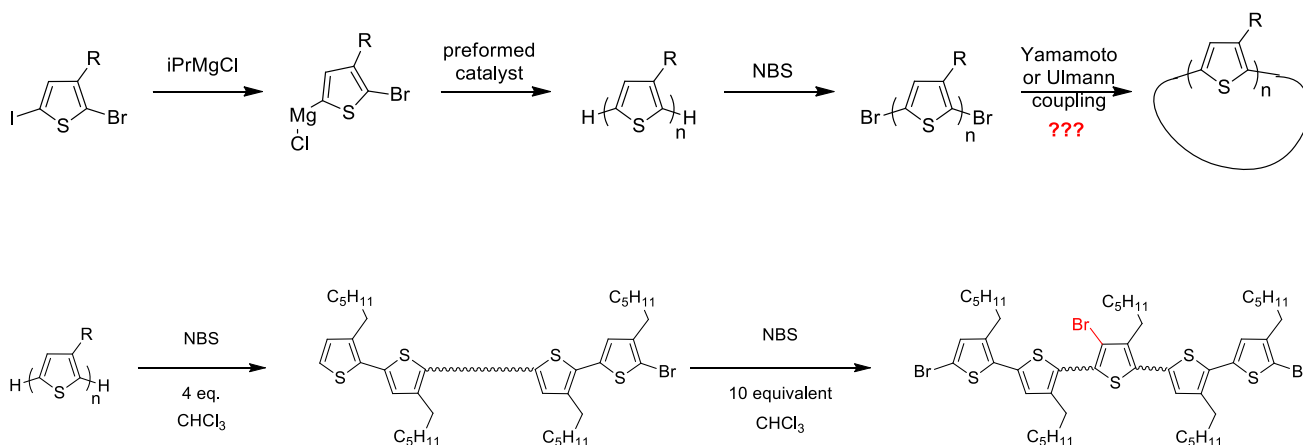
A perceived difficulty in the synthetic pathway of α,ω-brominated regioregular polythiophenes was the possibility of bromination in the chain (overbromination). All polymers were extensively characterized by 1H NMR spectroscopy – here we show the chemical structure of the polymers with an indication of possible overbromination and the chemical shifts of end chain protons (red)
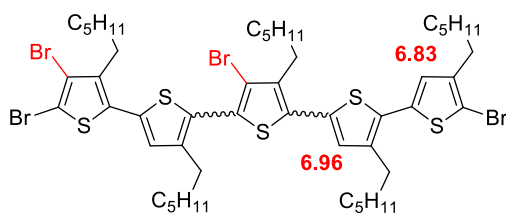
So, even with overbromination, the ring closure reaction was carried out using the Ulmann coupling and supposing that Ullman reaction can't occur in the middle of the chain. After the cyclisation reaction bromine was removed by treatment with LiAlH$_4$. The reaction of cyclisation according to Ullman mechanism with a modified catalyst CuTc (Cu complexed with thiophene carboxylate acid) gave a fully conjugated regioregular alkylthiophene macrocycle. Potential side reaction and proper isolation of the macrocycle from addition polymers is still a (not yet fully resolved) issue.
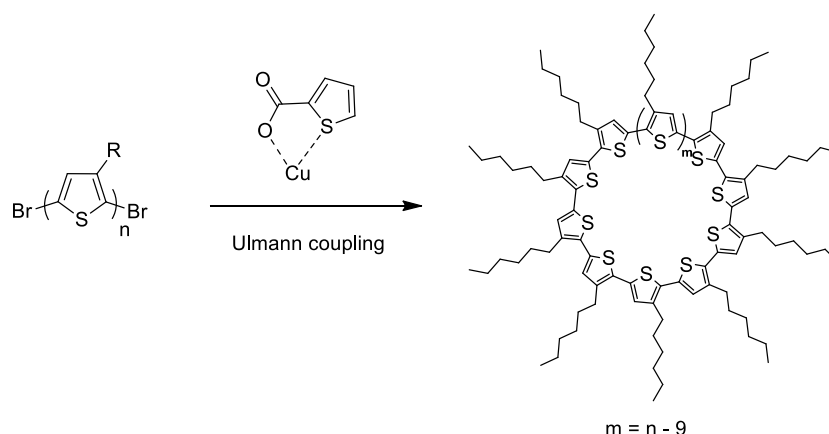

Table: Typical conditions and results for the first trials.

Macrocycle	Concentration in THF	temperature	equivalent of CuTC (mass)	Mp linear system (kDa eq. PS standard)	Mp after cyclisation (kDa eq. PS standard)
NIDE A078	59 mg in 60mL in 500 mL	45°C	4 (7.2 mg)	10600	10400

To circumvent problems with overbromination and facilitate the Ullman coupling, iodination of regioregular polythiophenes was tried but it appears almost impossible to iodinate the alpha position of polymer with classical NIS, as inferred from NMR spectra.

NIS

4 eq.

CHCl$_3$ / MeOH

R

X
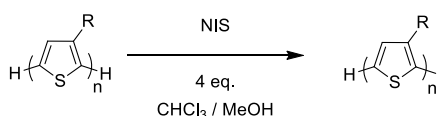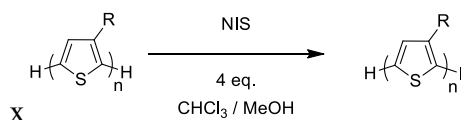
A new idea currently tested is the use of a very steric hindered base to deprotonate the first thiophene of the chain before addition of I$_2$ or Br$_2$.

1. Base

2. I$_2$

x eq.

Solvent

TMP-Li=
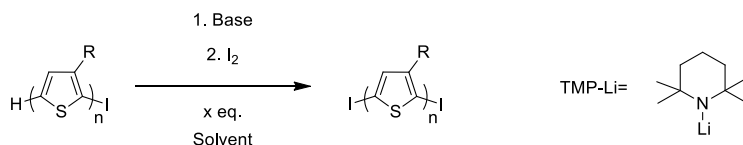
Double defect macrocycles, i.e. macrocycles with a defect in the regioregularity have also been synthesized starting from single defect polythiophene. Here iodination of the polymer chain ends was successful and allowed to increase the reactivity towards Ullmann coupling.

C$_6$H$_{13}$

NIS

CHCl$_3$ / MeOH

C$_6$H$_{13}$

C$_6$H$_{13}$
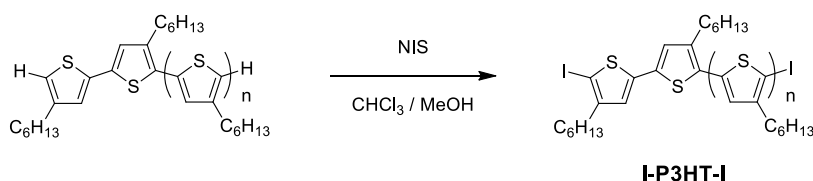
I-P3HT-I

These end-iodinated polymers (I-P3HT-I) were undergoing a cyclisation reaction in THF with CuTC as catalyst (conditions: 45°C in THF in *high diluted* solution with an addition of polymer solution over 18 hours (110 mg in 110 mL added to 500 mL of THF containing 13 mg of catalyst (4 equivalents)). The high dilution is a requirement to avoid intermolecular chain addition and favoring cyclisation:

C$_6$H$_{13}$

Br

Br

C$_6$H$_{13}$

C$_6$H$_{13}$

Ulmann coupling
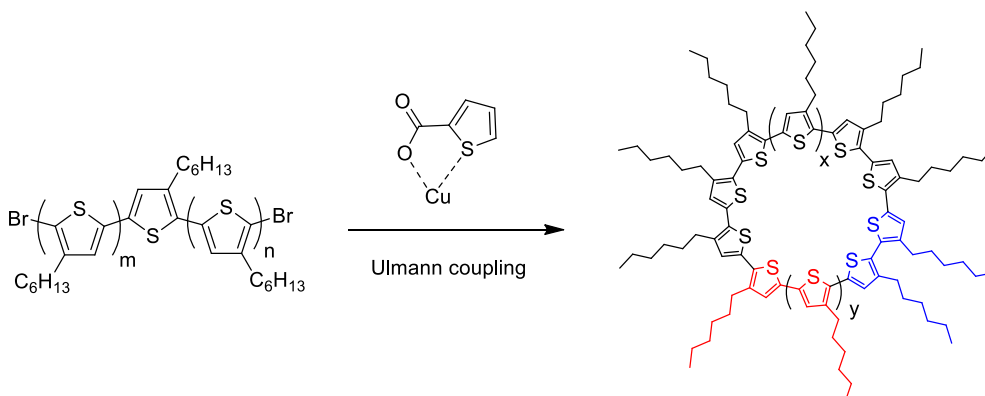
Measurements of Faraday rotation.

Our measurements of Faraday rotation are following rather standard techniques, as described in previous projects, albeit the new experimental set-ups have a very high sensitivity. All results on Faraday rotation are expressed in the value of the Verdet constant according the well-known equation:

$$\theta = V L B$$

here θ is the angle of rotation of the plane of polarization, the Faraday effect proper, L the sample length and B the magnetic field component parallel to the light beam. V, the phenomenological constant of proportionality, is the Verdet constant and a measure of the quality of the material for Faraday rotation applications.

An extensive program of measurements of the Faraday rotation in films of polymers synthesized was undertaken. A most vexing observation and repeatedly encountered problem was the poor reproducibility of the results – from very high Verdet to almost negligible! However it became clear that this is due to the morphology of the films, strongly dependent upon film preparation. An important clue to resolve this problem came from measurement of Faraday rotation in solution of a poly(3-octylthiophene). It was obvious that aggregation, induced by a bad solvent (CH_3OH) has a most deleterious effect – see Fig. 2
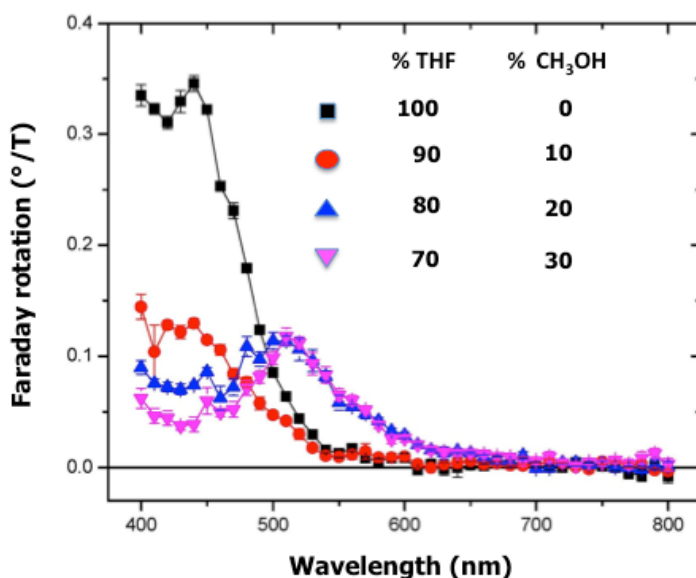

Figure 7. Faraday rotation in poly(3-octylthiophene) in THF/methanol mixtures (good/bad solvents) (.25 mg/ml)

From the measurement Faraday rotation measured from a $CHCl_3$ solution poly(3-octylthiophene) of we could estimate a very favorable Verdet constant of 10^6 °/Tm, assuming no interactions between the chains.
It is thus becoming increasingly clear that the morphology of the polymer films, amorphous or crystalline, is playing an important role in the Faraday rotation from

such films. We therefore started the synthesis of statistical regioregular copolythiophenes (statistical distribution of alkyl pendant chains, e.g. ethylhexyldodecylthiophene copolymers - see synthesis).

Surprisingly the Faraday rotation in films of polyselenophenes showed a low value for the Verdet constant. This may be in accordance of our observations of the poor reproducibility of Faraday rotation in polythiophene films. This is linked to morphology of the films – amorphous or crystalline – another important argument to concentrate research upon the role of aggregation effects on the Faraday rotation.

A most interesting, and for this project, experiment was the measurement of the Faraday rotation of a macrocycle of thiophene, the "Coulembier" macrocycle. macrocycle of poly(3-hexylthiophene). The measurement in chloroform solution indicated a very high Verdet constant for this macrocycle, in the order of 10^5 °/Tm – again assuming no interaction between the macrocycles in solution, which may be better realized for macrocycles as compared to linear polythiophenes.
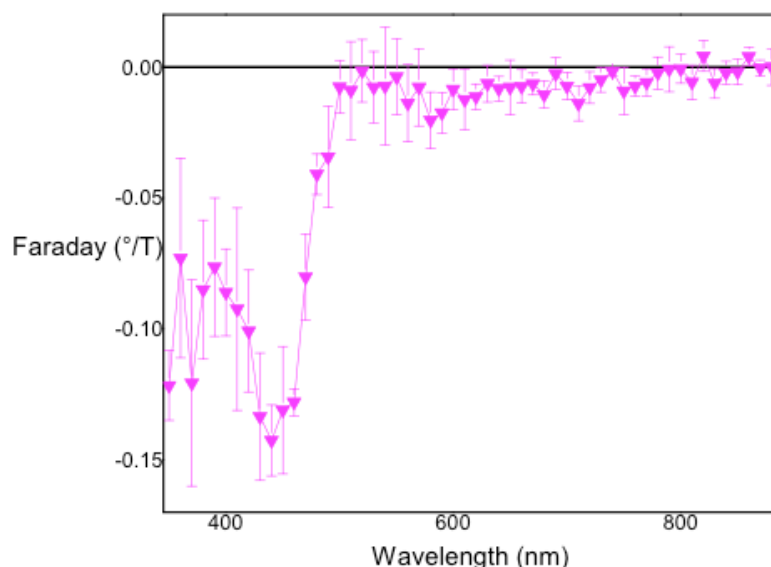

Figure 8. Faraday rotation of the "Coulembier" macrocycle in CHCl$_3$ (0.7 mg/ml)

Due to the low yield of the synthesis not enough material is yet available for the preparation of films to assess the Faraday rotation, and the reproducibility, of this very new magneto-optic material.

Ferromagnetism in polythiophenes

A first and very important result in our investigation of magnetism in polythiophenes, and which gave new insight into the ferromagnetic properties of these conjugated polymers was obtained from the comparison of ESR measurements with SQUID magnetometry measurements on a chiral

polythiophene, poly(S-3,7-dimethyloctylthiophene) [S. Vandeleene et al., Macromolecules 2011, 4911-4919]. Here it was shown that there is a marked discrepancy between the spin density measured from ESR and the number of Bohr magnetons as obtained from SQUID measurements – See the Table giving the ratio of spin density and the numbers of Bohr magnetons for polymers of different molecular weight.

Table: Comparison between Spin density (ESR) and Bohr magneton (SQUID)

polymer	spin density $(10^{16}$ spins/g$)$	Bohr magnetons $(10^{17}/g)$	ratio
$\overline{M}_n = 7.0$ kg/mol	1.3	3.1	0.041
$\overline{M}_n = 12.5$ kg/mol	1.2	3.1	0.039
$\overline{M}_n = 16.0$ kg/mol	2.5	1.7	0.155

These results point clearly to the presence of an additional spin system not resolved by ESR and indicative of orbital magnetism. This may explain the hysteresis effects observed SQUID magnetometry in polythiophenes. It should be noted that these results do not imply necessarily a relation between (orbital) magnetism and chirality since the hysteresis effects are observed in chiral as well as achiral samples. These results support also strongly our hypothesis of the role of cyclic structures.

Theoretical developments

The question, most central to this research, is the link between the doughnut structure and the magnetic properties observed. In a first approach we assumed that fluctuating currents in a annular conducting structure, the nanodoughnut, give rise to a fluctuating magnetic moment which may have a large value, e.g. of the order of 100's of Bohr magneton with the size of the doughnut ring.
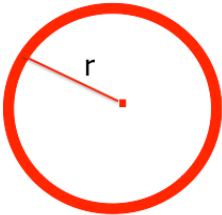
Figure 9. The nanodoughnut as a nanomagnet. For the speed of the fluctuating electron we arbitrarily assumed the Fermi velocity in a metal. The geometrical details are from the AFM picture of the nanodoughnut.

A most exciting recent development was the recognition of the many similarities between our experimental results in poly(3-alkylthiophenes) on their magnetic properties and the results obtained for the magnetic properties of gold nanoparticles. This strongly supported our proposition about circulating currents in the nanodoughnuts as a potential source of large (fluctuating) magnetic moments in nanosized structures of (semi)conducting polymers.

As a result of this observation we started the investigations of the possibility of persistent currents in nanorings of conducting polymers to be compared with the persistent currents experimentally observed in one-dimensional metal rings, e.g. copper. Indeed, the requirements for the presence of a persistent current may be met in annular nano-structures of pristine, highly regioregular poly(3-alkylthiophenes: (a) small ring size to preserve phase coherence of the electron(s), (b) absence of localization of the electron in the ring (no oxidative defects) and (c) no inelastic scattering due to structural defects.

As a first model to investigate the possibility of persistent (or fluctuating) currents in organic macrocycles we addressed the particle-on-a-ring, an circular analogue to the well-known particle-in-the-box.

$$\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial^2\varphi}{\partial\theta^2} = -E\,\varphi$$

$$\varphi = \frac{1}{\sqrt{\pi}}\sin nb$$

$$E = n^2\frac{\hbar^2}{2\,mr^2} \quad \text{with} \quad n = 0,\ \pm1,\ \pm2,\ \pm3,....$$

Figure 10. the particle-on-a-ring, wave functions and energy levels – remark the great analogy with the particle-in-the-box.

Taking a 1-D ring of 10 thiophenes, $r \approx 10$ nm, the HOMO-LUMO energy difference being in the order of $k_B T$ – making an electron in the HO rbital essentially free – we estimate the electron velocity (from the kinetic energy of the HO electron) as about 10^4 m/sec. This would give a magnetic moment for the ring in the order of 1 bohr magneton.

A further extension to 2D and 3D – a *torus* - would yield better estimates. This was tried but turned out to be a most intricate and extremely difficult problem since the Schrödinger equation is not separable in a toroïdal symmetry. In literature we could not find information on this problem. Approximation methods will be needed to obtain a description of electron wave functions and eigenvalues in such toroïdal structures. Some numerical calculations have been carried out by Roger Evrard, University of Liège, Belgium, based upon very simple approximations for an isolated electron in a torus with reflecting walls.

Simulations.

To further investigate macrocycles of conducting polymers we initiated an extensive program of simulations of structure and properties. These simulation/modeling of the properties of annular structures were carried out in close collaboration with the Dr. Palash Gangopadhyay, University of Arizona, Tucson, USA.

A first simulation/modeling, using DFT –B3LYP- CEP 3G* optimized, was carried out to obtain some insight into the properties of a Coulembier ring. In view of the needed computer time the ring simulated was a 12 ring with the aldol condensation closure. Some very interesting results could be obtained, as shown in Figure 11.
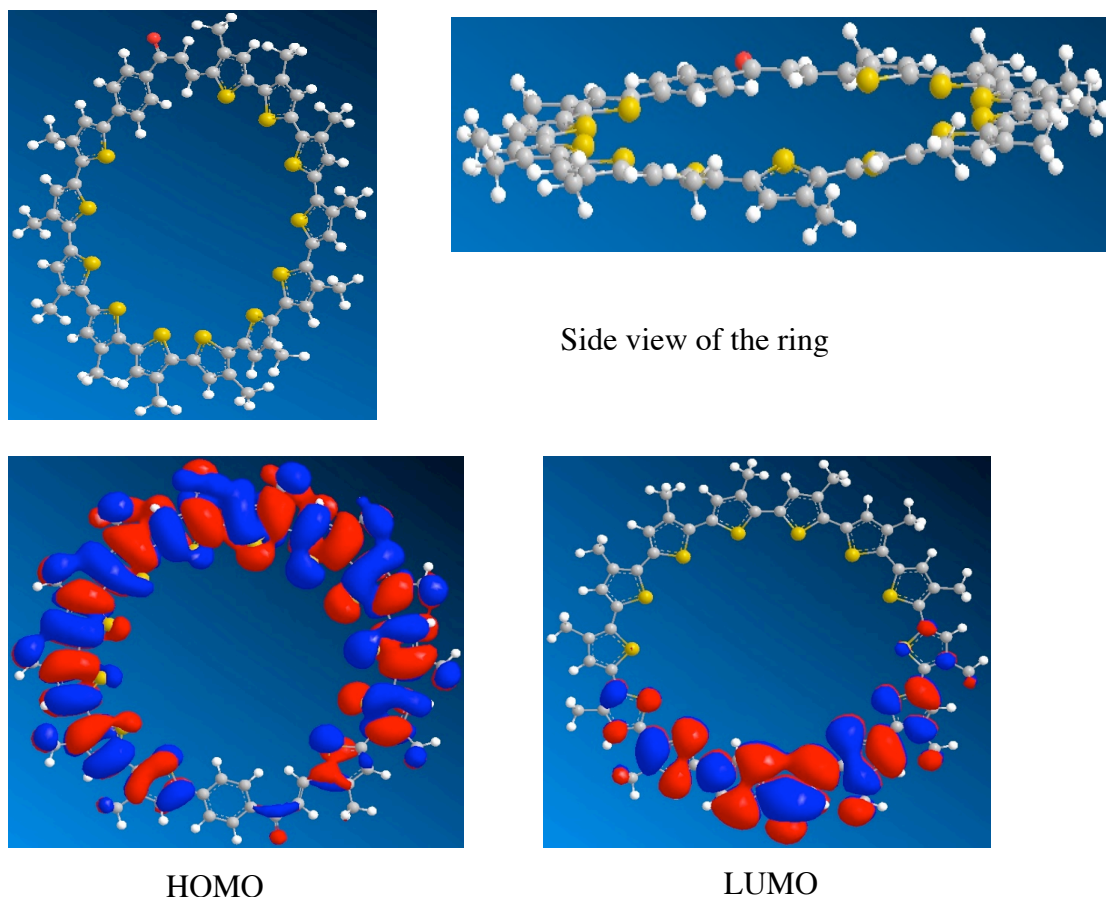

Side view of the ring

HOMO   LUMO

Figure 11. Optimization of the ring structure, and HOMO and LUMO levels.

From these calculations we see that this simplified "Coulembier" ring is rather flat. Also, from the HOMO and LUMO levels we see that this ring, with the breaking of conjugation by the closure, could possibly be approximated as a "split ring" with exciting applications as a metamaterial.
In view of the electronic density as calculated we also calculated the dipole moment of this ring, with a remarkable result as shown in Fig. 12.
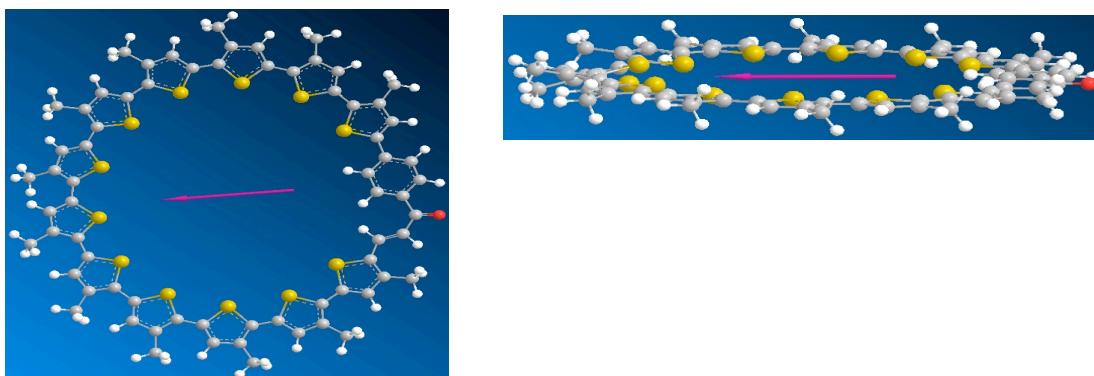
Figure 12. The dipole moment of the "Coulembier "ring

As seen from figure 12 the dipole moment, calculated as 7.12 Debye, is very large and lying in the plane of the ring. We started to calculate the possibility of stacking of the rings due to an antiparallel aggregation. Indeed, a very interesting result from these calculations is that docking another ring, with dipoles antiparallel, the steric hindrance will force the two rings to slightly move away from antiparallel orientation and this will cause a slowly helical morphing of dipoles in a single stack, hence the introduction of helicity and a way of realizing chiral stacks of conducting rings, of some importance for the generation of spin-polarized currents.

Other simulations and modeling were carried out on the new rings of polythiophenes with complete conjugation and regioregularity. For computer-time reasons we restricted the rings to 10 methylthiophenes, although much larger rings are synthetically available. The simulation results are shown in Fig. 13.
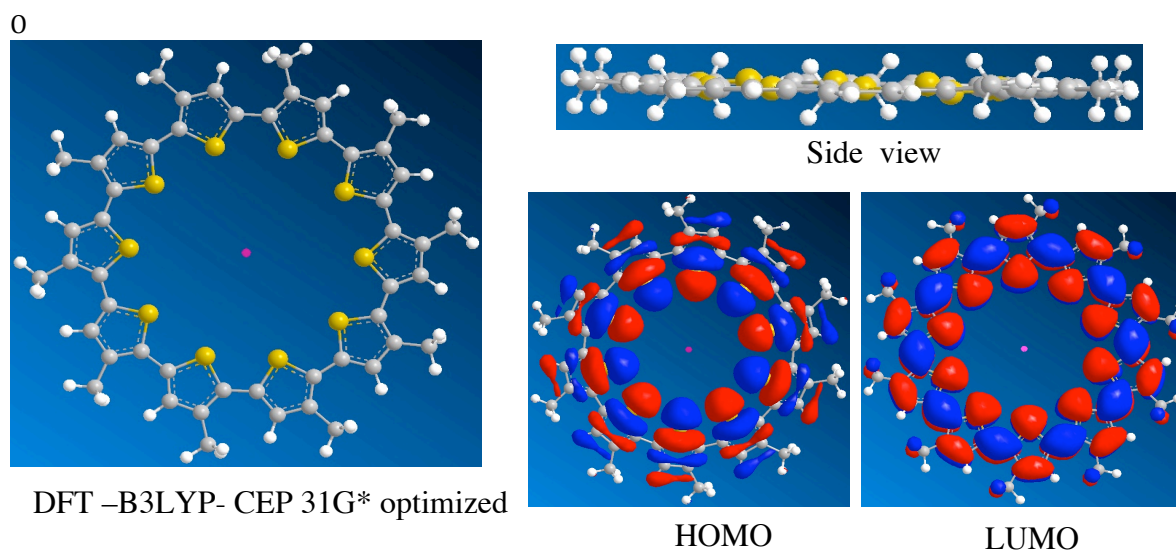
0

Side view

DFT –B3LYP- CEP 31G* optimized

HOMO   LUMO

Figure 13. Optimized structure and energy levels for a decamethylthiophene ring with perfect regioregularity. The violet dot, is the dipole vector projecting upward from the center of the ring, computed dipole ~0.7 Debye.
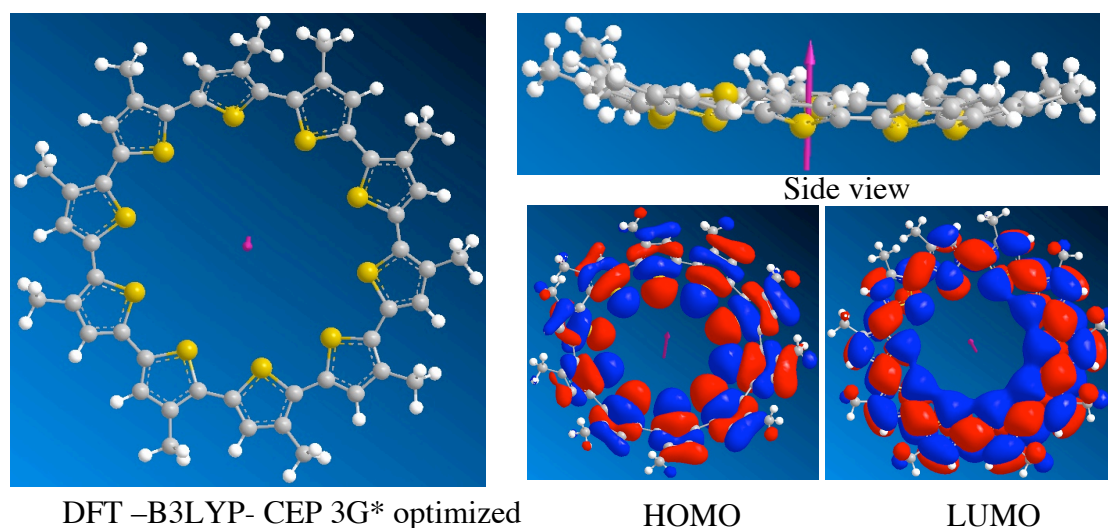
| DFT –B3LYP- CEP 3G* optimized | HOMO | LUMO |

Figure 14. Optimized structure and energy levels for a decamethylthiophene ring with a defect in the regioregularity. The violet dot, is the dipole vector projecting upward from the center of the ring, computed dipole ~4.45 Debye.

For the record, the IUPAC names of these two rings are:
$1^3,2^4,3^4,4^4,5^4,6^4,7^4,8^4,9^4,10^3$-decamethyl-1,2,3,4,5,6,7,8,9,10(2,5)-decathiophenacyclodecaphane (perfect regioregularity), and
$1^3,2^3,3^3,4^3,5^3,6^3,7^3,8^4,9^4,10^3$-decamethyl-1,2,3,4,5,6,7,8,9,10(2,5)-decathiophenacyclodecaphane (defect regioregularity)

It is interesting to see that the perfect ring is very flat – from the dipole moment of 3-methylthiophene and the calculated dipole moment it can be derived that the thiophene rings are out of the plane for about 6°. In contrast the defect ring has a much larger dipole moment in accordance with the cup form of the ring.

We also give here a summary of other results obtained for these rings:
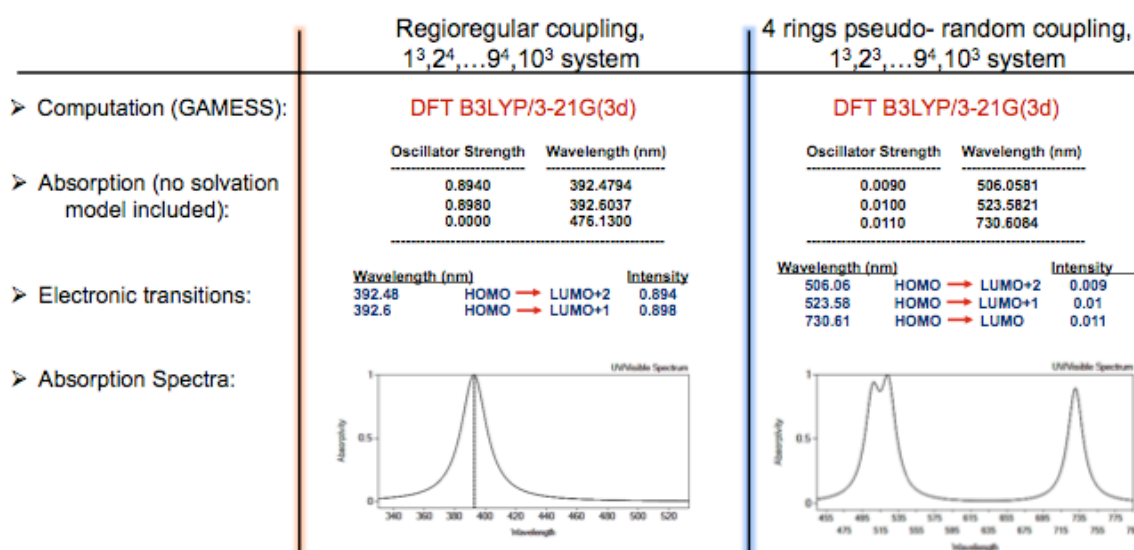
It is a remarkable result - as yet unexplained – that the oscillator strengths of the perfect regioregular and the regiodefect ring are so different. The absorption appearing in the defect ring is probably due to a defect level between HOMO and LUMO levels. This would be potentially important for the appearance of persistent currents in such organic conducting rings – a phenomenon well known in metal rings but never shown in organic rings.

These calculations are now used as an important feedback to the synthetic chemists – for example, the potential stacking of "Coulembier" rings into a chiral structure is now an important incentive for the synthesis of a Coulembier ring with a chiral side-group.

The calculations show also the potential of these new materials, not only for magneto-optics (Faraday rotation) but also for organic magnetism (persistent currents) and metamaterials in the UV-Vis regime.

CONCLUSION and REALISATION of OBJECTIVES.

In this project we developed an extended portfolio of polythiophenes, achiral as well as chiral, which have been thoroughly characterized in their chemical properties.

Faraday measurements on these polymers, in solution and thin films, have clearly shown the great potential of these polymers as materials for magneto-optical applications. An intense research effort of several excellent teams, at several universities, has set the stage of a worldwide interest in (nonlinear) magneto-optics, as witnessed by many invitations of the PIs and collaborators to international meetings. The results of this project have also opened a new way to organic magnetism of environmental stable polymers, while on a more theoretical way the study of persistent currents in organic cyclic structures has been initiated.

The availability of well-characterized polythiophenes and macrocycles of thiophenes will allow the experimental investigation of the magnetic properties of these materials by SQUID measurements – a dedicated SQUID instrument will become available in the near future.

Other topics to explore, some ongoing already, as a sequel to this project are the development of a quantum chemical model of toroïdal organic structures, the simulation of macrocycles and cyclic and helical structures by advanced DFT methods such as CDFT (Current) and BDFT (Magnetic field) which allow the description of magnetic properties, theoretical and experimental investigations of the relation between chirality and magnetism, the development of chiral stacks from macrocycles as advanced materials for the generation of spin polarized currents, the potential of "split" organic macrocycles as metamaterials…

References

We give here the general references which are the basis of his project. Publications on the results of this project are forthcoming, e.g. Proc. SPIE 2014.

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